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Effect of bath temperature on optical and morphology properties of CdS thin films grown by chemical bath deposition

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Abstract

Synthesis of CdS thin films were carried out onto glass substrates by chemical bath deposition (CBD) method using $\text{CdCl}_2 \cdot 8\text{H}_2\text{O}$ and thiourea as S^{2-} ion source with ammonia as a complexing agent. Influence of bath temperature on structural, morphology and optical properties has been systematically and carefully investigated. XRD analysis revealed that the synthesized CdS films are nanocrystalline having hexagonal structure with (002) preferential orientation. Estimated crystallite size was found in the range 16–32 nm. The UV-Visible spectroscopy analysis showed that the films have high transmission (> 70 %) in visible and NIR region of solar spectrum. Optical band gap was found > 2.3 eV over the entire range of bath temperature studied. The Raman spectra for the CdS films deposited at various bath temperatures shows a continuous shift of 1 LO phonon peak towards higher frequency which suggest the improvement of structural order with increase in bath temperature. The increase in the intensity ratio, 2LO/1LO with bath temperature indicates enhancement of crystallinity of CdS films with increase in bath temperature. The SEM analysis showed that CdS films deposited at various bath temperatures are smooth, homogeneous, and nearly uniform with randomly oriented spherical nanocrystallites.

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1. Introduction

Cadmium sulphide (CdS) is a semiconductor with a direct band gap of 2.42 eV. Research activity on CdS was started in early 1950s when *Reynolds et al.* [1] first observed the photovoltaic effect in single crystal CdS with various metalelectrodes. In recent years there has been growing interest in CdS thin films compare to its bulk counterpart due to excellent properties such as tunable band gap (2.1-2.45 eV) [2], high carrier concentration (10^{16} - 10^{18} cm⁻³) [3] and mobility (0.1-10 cm²V⁻¹s⁻¹) [4], high absorption coefficient ($> 10^4$ cm⁻¹), high electrochemical stability [5] etc. The material has been successfully employed in chemical sensor [6], surface acoustic wave devices [7] and photo-anode films of solar cells [8,9], thin film transistors (TFT), photocatalysis and biological sensors [10], optical coding, optical data storage and sensing [11, 12], non-linear integrated optical devices [13, 14]. As per as solar cells are concerned, CdS has been used as a window material together with several semiconductors such as CIGS, CZTS, CdTe, Cu₂S etc. based solar cells [15-17].

For the deposition of CdS thin films both gas phase and liquid phase methods have been used. Gas phase method includes vacuum evaporation [18], flash evaporation [19], molecular beam epitaxy (MBE) [20], sputtering [21] and screenprinting [22], pulsed laser ablation (PLA) [23] whereas liquid phase method includes electrodeposition [24], successive ionic layer adsorption and reaction (SILAR) [25], chemical bath deposition (CBD) [26], chemical spray pyrolysis (CSP) [27] etc. Each deposition method has its own advantages and limitations. Among these, chemical bath deposition method has many advantages over the others such as its simplicity, cost effectiveness, possibility of large area deposition, minimum material wastage and no need to deal with poisonous gases and no requirement of costly sophisticated instruments. Furthermore, properties of CdS thin films can be controlled easily by varying various process parameters. However, capabilities of chemical bath deposition for obtaining device quality CdS have not been fully established and only few reports on dependence of bath temperature on properties of CdS films exist in the literature. With this motivation an attempt has been made to investigate the effect of bath temperature on properties of CdS thin films by chemical bath deposition method.

2. Experimental details

2.1. Film preparation

The cadmium sulfide (CdS) thin films were prepared by chemical bath deposition (CBD) method using cadmiumchloride (CdCl₂) as a cadmium source (0.1 M), thiourea [SC(NH₂)₂] as a sulphur source (0.1 M), and ammonia. Fig. 1 shows the schematic of CBD method used in the present study.

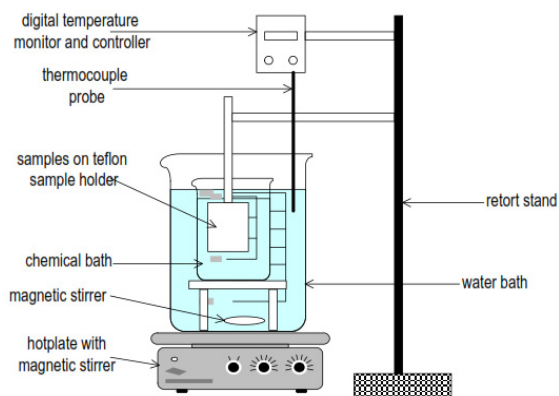


Fig. 1. Schematic of chemical bath deposition (CBD) method used in the present study for deposition of CdS films.

The glass substrates were initially clean with soap solution, double distilled water, ethanol, acetone and finally an ultrasonic cleaning for 20 min in double distilled water. Deposition temperature (bath temperature) was varied from 65°C to 85°C at an interval of 10°C while other process parameters being kept constant and are listed in Table 1.

Table 1. Deposition parameters employed for the synthesis of CdS films

Deposition Parameters	Values
Cadmium Chloride (CdCl ₂)	0.1 M
Thiourea [SC(NH ₂) ₂]	0.1 M
pH of the bath	11.5
Deposition Time (Minute)	40
Deposition Temperature (°C)	65-85

2.2. Film characterization

Raman spectra were recorded with Raman spectroscopy (Jobin Yvon Horibra LABRAM-HR) in the range 100-1200 cm⁻¹. The spectrometer has backscattering geometry for detection of Raman spectrum with the resolution of 1 cm⁻¹. The excitation source was 532 nm line of He-Ne laser. The power of the Raman laser was kept less than 5 mW to avoid laser induced crystallization on the films. X-ray diffraction pattern were obtained by x-ray diffractometer (Bruker D8 Advance, Germany) using Cu K_α line ($\lambda = 1.54056 \text{ \AA}$). The patterns were taken at a grazing angle of 1°. The average crystallite size was estimated using the classical *Scherer's* formula [28]. The optical band gap of the CdS films was deduced from transmittance and reflectance spectra of the films deposited on glass and were measured using a JASCO, V-670 UV-Visible spectrophotometer in the range 300-1200 nm. The surface morphology of the films is investigated using scanning electron microscopy (JEOL JSM-6360 A). Thickness of films was determined by profilometer (KLA Tencor, P-16+).

3. Results and Discussion

3.1. Variation in film thickness

The CdS thin films have been deposited using the chemical bath deposition method and the thickness are measured using electro-mechanical contact Talystep surface profilometer (KLA Tencor, P-16+). The variation of film thickness as a function of bath temperature is shown in Fig. 2.

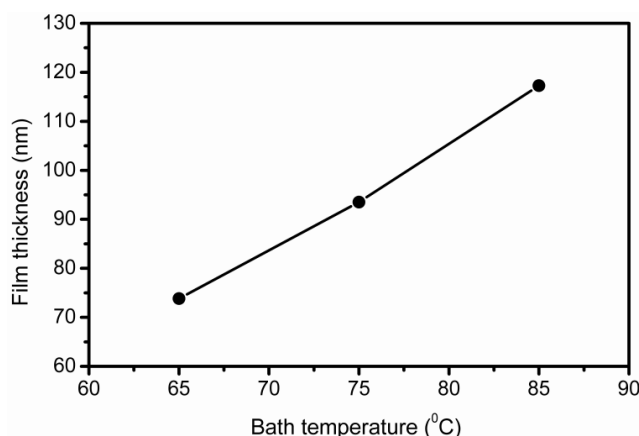


Fig 2. Thickness variation of CdS thin films deposited at different bath temperatures

As seen from the figure, the film thickness linearly increases with increase in bath temperature. It increases from 73.84 nm to 117.28 nm when the bath temperature increased from 65 °C to 85 °C. It has been reported that too thick CdS films lead to the reduction of photon into the absorber layer, while too thin is hard to synthesize smooth films with few pinholes [29]. However, in the present study we have successfully controlled the CdS film thickness simply by controlling the bath temperature in CBD method.

3.2. Low Angle XRD Analysis

Low angle x-ray diffraction (XRD) is a multipurpose, non-destructive technique which gives direct information about crystallographic structure of materials. Fig. 3 shows the XRD pattern of CdS thin films grown by CBD at different bath temperatures.

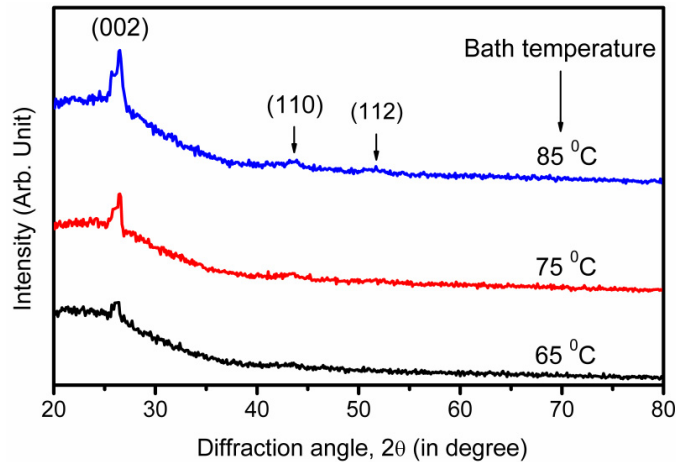


Fig. 3. Low angle x-ray diffraction pattern of CdS thin films deposited at different bath temperatures.

As seen from the figure, CdS film deposited at 65 °C shows only a broad peak centered near $2\theta = 26.5^\circ$ which corresponds to (002) plane. With increase in bath temperature to 75 °C the XRD pattern shows a moderately intense peak at $2\theta \sim 26.5^\circ$ and an additional broad peak centered $\sim 2\theta = 43.7^\circ$ which can be assigned (110) planes of the CdS. Finally, the CdS film deposited at 85 °C, three distinct peaks at $2\theta \sim 26.5^\circ$, 43.9° and 51.7° corresponding to (002), (110) and (112) planes of CdS can be clearly seen. According to standard JCPDS data card # 41-1049, these peaks correspond to hexagonal CdS [30]. The CdS films deposited at various deposition temperatures clearly show that these films have (002) preferred orientation of crystallites. This preferred orientation may be due to the controlled nucleation occurring in the film growth process [31]. It is therefore concluded that preferred oriented CdS films can be prepared by chemical bath deposition method by controlling the bath temperature. The crystallite size estimated using the classical Debye-Scherrer formula is listed in Table 2. It is seen that the crystallite size increases with increase in bath temperature for CBD deposited CdS films.

3.3. Raman Spectroscopy Analysis

Raman spectroscopy is one of the most sensitive tools for information on the local bonding configurations including crystallinity and structure disorders in lattice as well as using this we can understand phase transition [32]. Fig. 4 shows first order Raman spectra of CdS thin films deposited by chemical bath deposition at various bath temperatures. The Raman spectra of CdS thin films prepared at different deposition temperatures represent a well resolved line at 304 cm^{-1} and 605 cm^{-1} corresponding to the first order scattering of the longitudinal optical (1 LO) phonon and the second order scattering of longitudinal optical (2 LO) phonon respectively [33, 34]. Similar lines for CdS films were observed by previously by other research groups [35, 36]. A slight and continuous shift of 1LO phonon peak towards higher wave number with increase in bath temperature suggests the improvement of structural order in the film [37]. The ratio of intensity of first order longitudinal optical phonon and the second order longitudinal optical phonon peak, (2LO/1LO) has been often used as an indicator in the evaluation of CdS crystallinity in the film [32].

In the present study, increase in the intensity ratio, 2LO/1LO with increase in bath temperature indicates enhancement of crystallinity of CdS films.

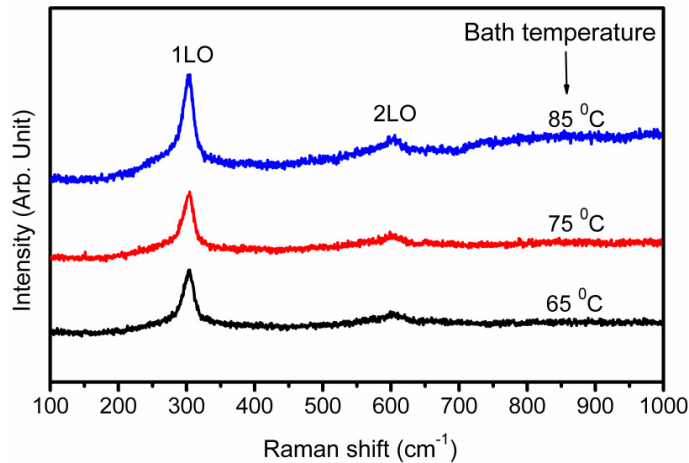


Fig.4. Raman spectra of CdS films deposited at different bath temperatures by chemical bath deposition.

3.4. UV-Visible Spectroscopy Analysis

Fig.5(a) show the UV-Visible transmittance spectra for CdS thin films prepared at different bath temperatures. As seen, all CdS thin films have high transmittance in visible and NIR region of solar spectrum (>70 %). Relatively high transmission of CdS films and sharp fall of transmission at band edge is an indication of low surface roughness and good homogeneity of the film [38]. Transmission in low wavelength region extends up to 300 nm indicate presence of disorders and amorphous components in the film [39]. There are few reports which have reported high transmittance of CdS films at high and low temperatures [40]. However, in present studies, high transmittance at lower bath temperature (85 °C) may be due to decrease in voids due to change bath temperature as well as improvement in uniformity, crystallite size and decrease in roughness with increase in deposition temperature.

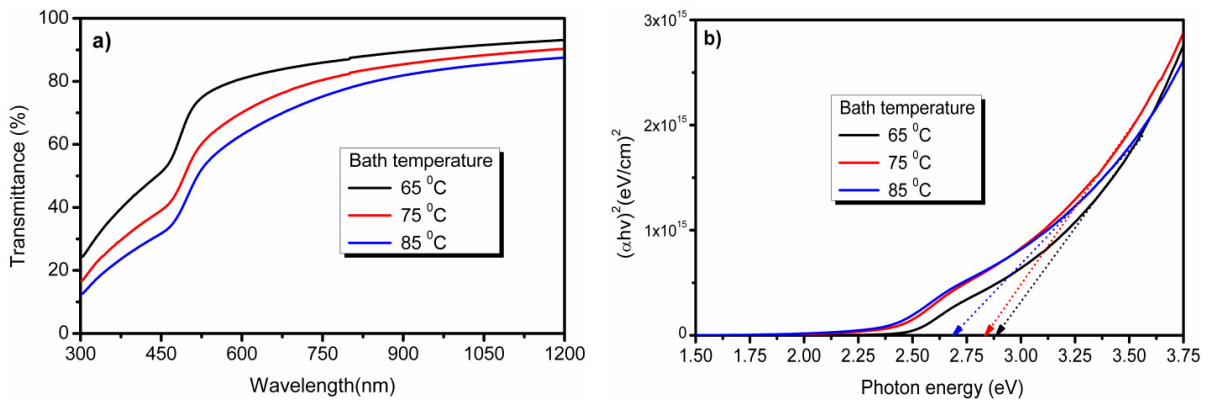


Fig.5. a) UV-Visible transmission spectra b) Tauc plot for the CdS films prepared at different bath temperature

The absorption coefficient (α) of CdS thin film was calculated from the transmittance spectra using Beer-Lambert approximation using relation [41],

$$\alpha = \frac{1}{d} \ln \left(\frac{I}{T} \right) \quad (1)$$

Where, α is absorption coefficient, d is thickness of the film, R is reflectance and T is transmission of CdS film.

Fig. 5(b) shows $(\alpha h\nu)^2$ versus $h\nu$ plot (Tauc plot) used to estimate band gap and Table 2 shows the estimated values of band gap from it.

Table 2: Estimated values of crystallite size and band gap at different bath temperatures for CBD deposited CdS films

Bath temperature (°C)	Crystallite size (nm)	Band gap values (nm)
65	16.4	2.89
75	20.3	2.83
85	32.7	2.59

As seen from the graph and Table 2 the optical band gap decreases with increase in bath temperature. Decrease in band gap can attribute to increase in crystallite size with increase in bath temperature. The larger crystallite size leads to an increase in absorption. As a result, the optical absorption edge shift towards longer wavelengths and consequently band gap decreases. Decrease in optical band gap with increase in bath temperature has been reported previously [40].

3.5. Scanning Electron Microscopy (SEM) Analysis

Figure 6 illustrates the scanning electron microscopy (SEM) micrographs of CdS thin films deposited at 65°C, 75°C and 85°C. As seen from the micrographs the surface morphology of all films is much smooth, uniform and crack free. The surface analysis indicates that the morphology of the CdS thin films changes significantly with increasing bath temperature. Small CdS grains are distributed uniformly over the entire substrate surface.

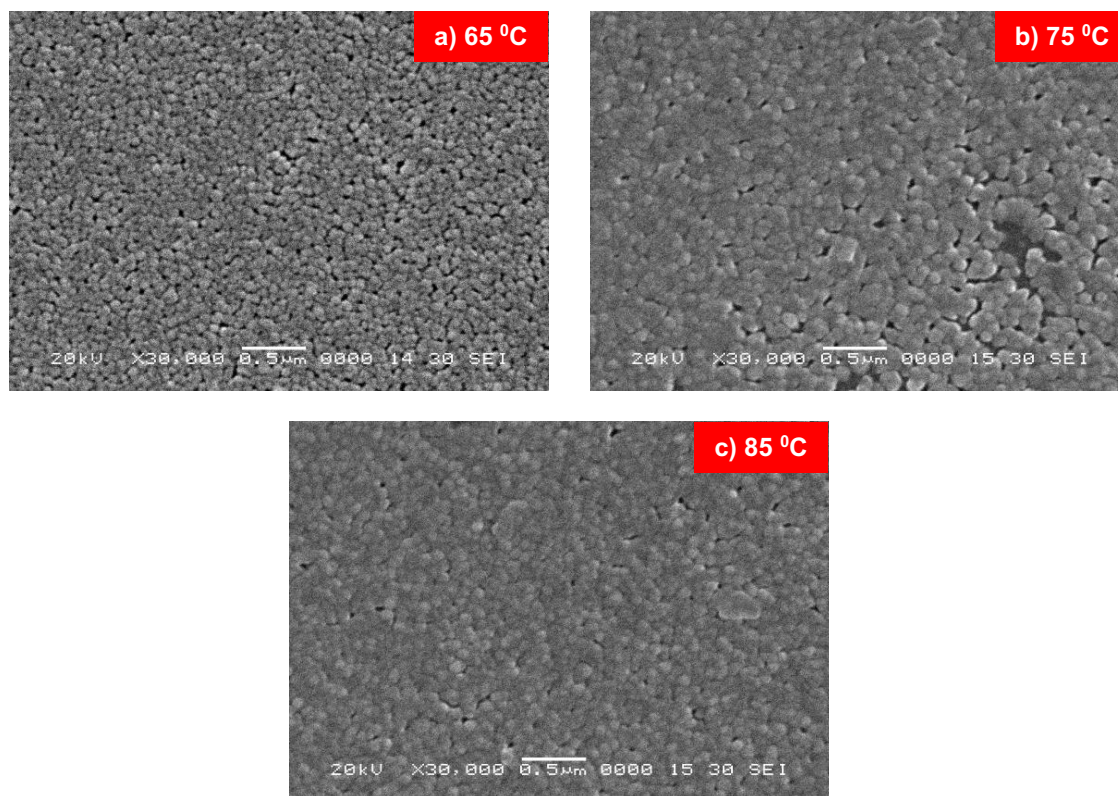


Fig. 6. SEM micrographs of the CdS thin films grown for different bath temperature **a)** 65°C, **b)** 75°C, and **c)** 85°C

The micrographs for the film deposited at 65°C show some pinholes and voids. However, with increasing deposition temperature the density of pinholes drastically gets reduced and the film deposited at 85°C become dense and almost pinhole free. Furthermore, some particles agglomerated resulting in protrusion can also be seen. Similar results have been reported by X. W. He [29].

4. Conclusions

In the present work, single step synthesis of CdS thin films has been carried out by chemical bath deposition method. The influence of bath temperature on the structural, morphological and optical properties has been investigated systematically. X-ray diffraction (XRD) analysis indicates the formation of crystalline hexagonal phase of CdS with (002) preferred orientation under the prevailing experimental conditions. Raman spectroscopy analysis revealed CdS phase purity. CdS thin films with good adherence have been obtained by CBD onto glass substrates. The SEM analysis showed that CdS thin films are smooth, homogeneous and uniform randomly oriented spherical nanocrystallites. The CdS thin films show high transmission in the range 600-1200 nm with the band gap > 2.6 eV. The bandgap energy values follow an inverse relation with crystallite sizes as expected from quantum size effects. Finally it has been concluded that the CBD grown CdS films can be useful as buffer layer in thin film solar cells.

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